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ORIGINAL ARTICLE

Direct production of dimethyl ether from synthesis gas utilizing bifunctional catalysts

Nahid Khandan · Mohammad Kazemeini · Mahmoud Aghaziarati

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Abstract In this study, direct synthesis of dimethyl ether from synthesis gas was investigated. For this purpose, H-mordenite zeolite was modified by wet impregnation of aluminum oxide onto it. The prepared catalysts were characterized by AAS, XRD and NH_3-TPD analyses. Results of catalytic tests indicated that H-mordenite modified with 8 wt% aluminum oxide was an appropriate catalyst for synthesis of dimethyl ether (DME) from methanol in which methanol conversion and DME selectivity were 99.8 and 96.8%, respectively, without a noticeable change in catalyst stability. A series of bifunctional catalysts, Cu–ZnO–ZrO_2/Al-modified H-mordenite, were prepared by co-precipitating sedimentation method and characterized. Synthesis of DME via direct CO hydrogenation was then evaluated in a three-phase slurry reactor. Experimental results showed that Cu–ZnO–ZrO_2/Al-modified H-mordenite was a suitable catalyst for the production of dimethyl ether from synthesis gas. Ultimately, the effects of operating conditions such as temperature, pressure and feed flow rate on the process performance of the determined optimum bifunctional catalyst have been reported.

N. Khandan · M. Kazemeini
Department of Chemical and Petroleum Engineering, Sharif University of Technology, Azadi Avenue, P.O. Box 11365-9465, Tehran, Iran

N. Khandan
Department of Chemical Industries, Iranian Research Organization for Science and Technology (IROST), Tehran, Iran

M. Aghaziarati (✉)
Faculty of Chemistry and Chemical Engineering, Malek Ashtar University of Technology, Lavizan, P.O. 15875-1774, Tehran, Iran
e-mail: maziarati@mut.ac.ir

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Introduction

Environmental pollution and its prevention are major problems that human beings have been concerned with for the past several decades. One main source of air pollution is gases leaving the exhaust of automobiles, in particular those from diesel engines. Dimethyl ether might be a very good replacement for diesel or LPG because it is a clean fuel (Arkharov et al. 2003). Dimethyl ether has been known to be a clean fuel with high cetane number, and low concentration of particulates and NO_x. For these reasons, it is a good candidate for replacing diesel fuel. In addition, DME might be utilized as a coolant replacing chlorofluorocarbons (Bobbo and Camporese 1998; Bivens and Minor 1998). Considering these advantageous applications and the fact that the price of crude oil has been rising steeply, the production and utilization of DME has become a realistic alternative (Good et al. 1999; He et al. 2003).

Dimethyl ether might be produced directly from methanol or indirectly from natural gas. In the latter process, first natural gas is reformed to synthesis gas, and then synthesis gas is converted into methanol or directly to DME. Synthesis of DME from synthesis gas (i.e., CO and H_2) is thermodynamically and economically more favorable than from methanol (Yaripour et al. 2005; Brown et al. 1991; Fei et al. 2004; Qi et al. 2001; Takeguchi et al. 2000; Li et al. 1996, 1997; Ge et al. 1998; Xia et al. 2004; Ramos et al. 2005; Jun et al. 2003; Rhodes et al. 2005; Rhodes and Bell 2005; Arena et al. 2007; Liu et al. 2001; Suh et al. 2000; Sun et al. 2003).

The principal reactions involved in the STD process are methanol synthesis, methanol dehydration and water gas shift (WGS) (Mao et al. 2006); i.e.

$CO + 2H_2 \leftrightarrow CH_3OH$	$\Delta H = -90.29$ kJ/mol	MeOH synthesis	(1)
$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$	$\Delta H = -23.41$ kJ/mol	MeOH dehydration	(2)
$H_2O + CO \leftrightarrow CO_2 + H_2$	$\Delta H = -40.96$ kJ/mol	WGS	(3)
$3CO + 3H_2 \leftrightarrow CH_3OCH_3 + CO_2$	$\Delta H = -244.95$ kJ/mol	Syngas to DME	(4)

The combination of these reactions results in a synergistic effect for relieving the unfavorable thermodynamics for methanol synthesis, because one of the products at each step is a reactant for another. This creates a strong driving force for the overall reaction, which allows a very high syngas conversion in one single pass.

A previous study by us indicated that modified zeolites were suitable materials to produce DME from methanol (Khandan et al. 2008). In addition, other investigations showed that Cu–ZnO–ZrO_2 was an appropriate catalyst to convert methanol to DME. Furthermore, recent studies have demonstrated that zirconia has a synergetic effect on DME production (Rhodes et al. 2005; Rhodes and Bell 2005; Arena et al. 2007; Liu et al. 2001; Suh et al. 2000; Sun et al. 2003; Mao et al. 2006).

In the present paper, we report the results of the direct synthesis of DME from syngas with a new bifunctional catalyst composed of Al-modified H-mordenite as a methanol dehydration component and Cu–ZnO–ZrO_2 as a methanol synthesis component in a slurry reactor. Utilizing this new catalyst in a slurry reactor is the major novelty of the present work. Also, the effects of operating conditions such as temperature, pressure and feed flow rate on the catalytic performance have been reported.

Experimental

Catalyst preparation

Mordenite zeolite was obtained from the Zeolyst Company (USA). Zeolite, as received, was in the Na form, was ion exchanged to the NH_4^+ form using an aqueous solution of NH_4NO_3 and was subsequently dried at 373 K for 24 h. H^+ form of zeolite was prepared by calcination of the NH_4^+ form sample at a constant rate of temperature rise (2 K/min) from 373 to 773 K while keeping the temperature at 773 K for 5 h. H-mordenite (HM), modified with aluminum oxide, was prepared by wet impregnation of H-mordenite with aqueous solutions of aluminum nitrate. In detail, an appropriate weight of aluminum nitrate ($Al(NO_3)_3.9H_2O = 2.352$ g) was dissolved in water (15 ml) under moderate stirring (300 rpm). Then, a specific amount of zeolite (7.6 g) was added to this solution and stirred under the aforementioned speed for about 1 h and left for 24 h at room temperature. After that, the suspension was dried at 383 K overnight and then calcined at 723 K for 3 h in an air stream to obtain zeolite of H-mordenite, modified with 8 wt% Al_2O_3.

In our previous study, we showed that the appropriate molar ratio of elements in the bifunctional catalyst (hydrogenation to dehydration) was 2:1 (Khandan et al. 2009). Therefore, bifunctional catalysts (Cu/ZnO/ZrO_2: 46/46/8 on Al-modified H-mordenite zeolite) were prepared with a molar ratio of 2:1 and using the co-precipitation sedimentation method (Ge et al. 1998). In short, the appropriate weights of metal nitrate and sodium carbonate solutions were added to 200 ml of deionized water simultaneously and drop-wise over a period of 30 min at constant pH (ca. 7.0) and temperature (323 K) with continuous stirring. After the mixture had been aged for 2 h under stirring at the same temperature, the resulting precipitates were filtered out and washed. To eliminate the effect of residual Na^+ on catalytic activity, the precipitates were washed with hot water (353 K) completely and then added to the suspension of Al-modified H-mordenite zeolite. The mixtures were stirred, filtered and dried at 393 K and later calcined in air at 673 K for 3 h.

Catalyst characterization

The BET specific surface area of the samples was measured by a multipoint N_2 adsorption–desorption method at liquid N_2 temperature (77 K) with a Micromeritics TriStar 3000 surface area analyzer. Samples were out-gassed under vacuum to remove the physisorbed water immediately before analysis.

The metal oxide content of the modified zeolites was determined by atomic adsorption spectroscopy (AAS) on a Perkin-Elmer AA 800 instrument.

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku D/MAX-1400 instrument with Cu–Kα radiation, with a scan speed of 15/min and a scan range of 4–70 at 40 kV and 40 mA.

Acidity measurements were performed by temperature-programmed desorption of ammonia (NH_3-TPD) with a conventional flow apparatus equipped with a thermal conductivity detector (TCD). An amount of the sample, 0.1 g, was pretreated in flowing helium at 773 K for 1 h, cooled to 423 K and then exposed to NH_3 (20 ml/min) for 30 min. Samples were subsequently purged with helium at

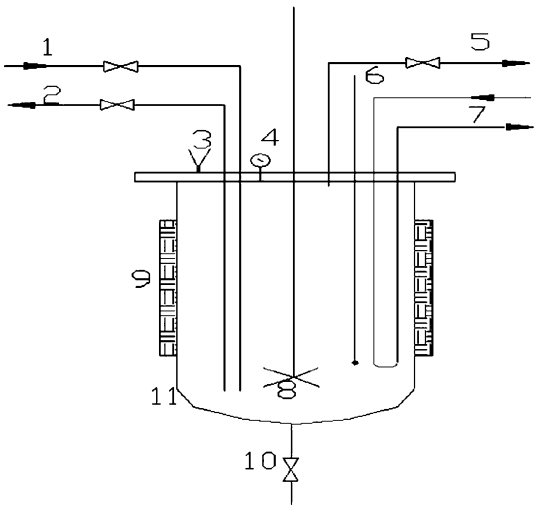

Fig. 1 Schematic of the batch reactor set-up constructed and used in this research; *1* gas inlet, *2* sampling valve, *3* slurry feed inlet, *4* pressure indicator, *5* gas vent, *6* thermocouple, *7* cooling coil, *8* stirrer, *9* reactor heating, *10* discharge valve and *11* reactor body

temperature (523 K) and turning the agitation on (at 1,000 rpm). The reaction was essentially a liquid-phase reaction with the solid catalyst suspended uniformly in the liquid medium in the form of slurry. The reaction duration was 3 h.

The analysis of the liquid product samples was carried out by using a gas chromatograph (Perichrom), equipped with an HP Pona Colon column (length = 50 m, ID = 0.2 mm) and flame ionization detector (FID), employing helium as the carrier gas. The injector and detector temperatures were set to 543 and 573 K; respectively. The column temperature program for this analysis was such that initially the column was kept at 308 K for 5 min. Then it was heated at a rate of 10°/min (from 308) to 503 K, at which it was kept constant for 30 min.

The material balance was found to be satisfactory. The error in this analysis was in the range of 3–5%. The activity and selectivity for various catalysts were calculated according to the following equations:

$$\text{MeOH conversion} = \frac{\text{MeOH moles (initial amount)} - \text{MeOH moles(final amount)}}{\text{MeOH moles (initial amount)}} \times 100 \quad (1)$$

$$\text{DME selectivity} = \frac{\text{DME moles produced} \times 2}{\text{MeOH moles (initial amount)} - \text{MeOH moles (final amount)}} \times 100 \quad (2)$$

the same temperature for 1 h to remove the physisorbed NH_3. The TPD measurements were conducted in flowing He (30 ml/min) from 373 to 973 K at a heating rate of 10°/min.

Catalytic reactions

Catalyst performance tests were carried out in a 500-ml autoclave. This reactor was equipped with a variable speed stirrer, cooling coil and PID controller. The maximum operating temperature and pressure were 623 K and 10 MPa; respectively. The experimental setup is shown in Fig. 1.

Experiments were carried out in two steps. First, the dehydration of methanol to DME was performed to examine the modified zeolite. In this way, to operate near isothermal conditions and to minimize catalyst deactivation effects, a known quantity of methanol (10 ml) was dissolved into the isooctane as the solvent (250 ml) and the resulting mixture was charged into the reactor along with a predetermined quantity of catalyst (3 g). The reactor was then flushed several times with nitrogen. The reaction was induced by bringing the reaction mass to the reaction

In the second step, the catalyst was suspended in liquid paraffin (i.e., treated to remove any trace poisons before use) with boiling point of higher than 340 °C. The catalyst was reduced in the autoclave reactor with diluted hydrogen (10% H_2 + 90% N_2) at a programmed temperature, rising from room temperature to 533 K. Then, it was kept at this temperature for 16 h. After this pre-treatment, syngas (H_2/CO = 2:1) was introduced into the autoclave under 50 MPa of pressure. The experimental condition and parameters are given in Table 1. All of the effluent gaseous products were analyzed by an online gas chromatograph

Table 1 Experimental conditions and reaction parameters employed in the current study

Parameter	Quantity
Temperature (K)	493–543
Pressure (MPa)	2.5–5.0
Catalyst (g)	3
Feed rate (ml/min)	100–400
Agitation (rpm)	1,000

Table 2 Physical characteristics of catalysts in this study

Zeolite	Metal oxide content (wt%)		BET surface area (m^2/g)	Total pore volume (cm^3/g) (%)	Mean pore diameter (nm)
	Nominal	Determined			
HM	–	–	500	0.204	2.805
Al-HM	8.00	7.97	275.1	0.168	4.91

using a carbon molecular sieve column and a TCD for hydrogen, carbon monoxide, carbon dioxide and methane, as well as a CP-Sil-5 column and an FID for DME, methanol and hydrocarbons.

Results and discussion

Investigation of dehydration catalyst performance

The results of catalyst characterizations are provided in Table 2. The content of aluminum oxide was determined by the AAS. Results showed that the metal oxide contents were consistent with those added before calcination, suggesting that no noticeable loss of these materials occurred during calcination.

The BET surface areas, total pore volumes and average pore diameters of the parent and modified HM zeolite are shown in Table 2. The BET surface area and total pore volume decreased in the modified zeolite, which might be attributed to the partial filling of zeolite pore with metal oxides.

X-ray diffraction patterns of the parent and modified zeolite are compared in Fig. 2. While the HM structural integrity was retained with the modification, nonetheless, the relative crystallinity decreased with impregnation of metal oxide. In addition, no crystalline metal oxide was detected through the XRD spectra. The above results indicated that the metal oxide undetected by the XRD might have been highly dispersed on the surface of the HM.

To understand the distribution of surface acidity and strength of acid sites, a systematic study of NH_3-TPD was undertaken. The quantitative estimation of acid sites and their region-wise strength distribution are shown in Table 3. The acidity of each peak was calculated according to the desorbed amount of NH_3. Three distinct regions were observed in acid profiles. In other words, three NH_3 desorption peaks were detected in the ranges of 100–300 °C (T_1), 300–500 °C (T_2) and 500–700 °C (T_3).

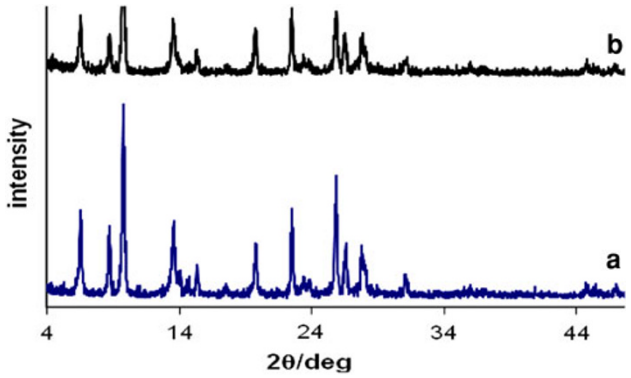

Fig. 2 XRD patterns of: *a* parent zeolite and *b* Al-modified HM zeolite

According to published data (Arena et al. 2007), the first peak (T_1) was assigned to desorption of NH_3 from weak acid sites, while the second peak (T_2) was due to desorption of NH_3 from moderate strength acid sites and the third peak (T_3) indicated the desorption of NH_3 from strong acid sites. In the current study, the area of the third peak (T_3) decreased slightly for the modified sample. Furthermore, the area of the second peak (T_2) increased expectedly for the Al-modified sample, implying that the amount of medium strength acid sites increased in the Al-modified HM.

The activity of HM and Al-modified HM, prepared via wet impregnation, is summarized in Table 3. The values, reported in this table, were averaged amongst three batches. It is observed that as the overall amount of the catalyst acidity increased, the conversion enhanced as well. In other words, conversion directly depended on the amount of catalyst acidity. On the other hand, it was found that selectivity was directly related to the sum of the weak and moderately strong acid sites. In other words, as this cumulative amount of strength was enhanced, the selectivity toward DME was increased.

To investigate the stability of the aforementioned catalysts, each one was used in several batches without any

Table 3 Results of NH_3-TPD analysis and catalytic tests over H-mordenite and Al-modified HM catalysts

Catalyst	Acidity (mmole NH_3/g cat)				Conversion (%)	DME selectivity (%)
	Weak	Medium	Strong	Total		
HM	0.271	0.332	0.254	0.857	96.4	68.2
Al-HM	0.338	0.541	0.067	0.946	99.8	96.8

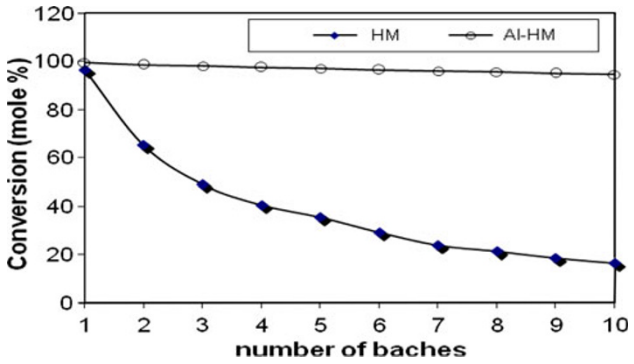

Fig. 3 Comparison of stability of applied HM and Al-modified HM catalysts

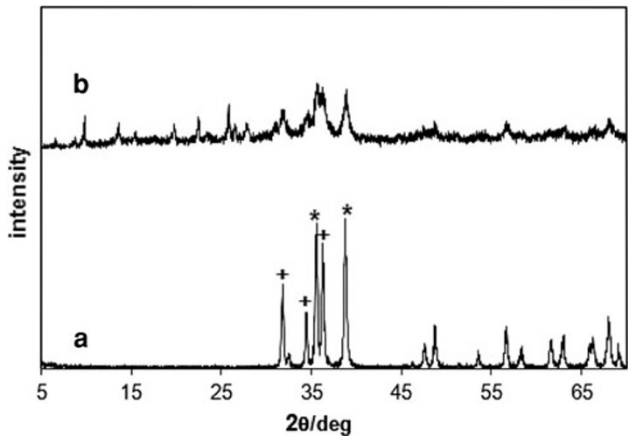

Fig. 4 XRD patterns of: *a* Cu–ZnO–ZrO_2 and *b* bifunctional catalyst Cu–ZnO–ZrO_2/Al-HM zeolite, (+) ZnO and (*) CuO

treatment. The results of catalyst performance are provided in Fig. 3. Methanol conversion decreased quickly with increasing number of batches in case of the parent HM catalyst, while in Al-modified HM catalyst methanol conversion was almost constant, indicating that the stability was clearly improved in cases of Al-modified HM catalyst.

Investigation of bifunctional catalyst performance

The XRD pattern of Cu–ZnO–ZrO_2/Al–H-mordenite catalyst is shown in Fig. 4. This catalyst exhibited diffraction peaks for CuO and ZnO. Besides the peaks assigned to CuO, ZnO and zeolite, no other peaks were observed to indicate the formation of new species between components.

Dimethyl ether synthesis was carried out utilizing a bifunctional catalyst composed of Cu–ZnO–ZrO_2 catalyst and the Al-modified H-mordenite zeolite with a weight ratio of 2:1. The performance of this catalyst has been summarized in Table 4.

The stability of the bifunctional catalyst, Cu–ZnO–ZrO_2/Al–H-mordenite, was investigated for direct DME synthesis via CO hydrogenation. The results are displayed in Fig. 5. These findings clearly showed that both the DME selectivity and the CO conversion remained essentially constant for the whole test duration, which confirmed that there was no substantial deactivation of the catalyst. These results revealed that the hybrid catalyst composed of Cu–ZnO–ZrO_2 and Al-modified H-mordenite with 8 wt% aluminum oxide had good stability for the direct synthesis of DME from synthesis gas.

The effect of operating conditions

Reaction temperature

The effect of temperature, as shown in Fig. 6, revealed that on increasing this parameter, there was an optimum value for CO conversion and DME selectivity. These optimum values occurred at a temperature near 523 K. The existence of these optima was due to the declined equilibrium value of CO conversion when temperature was raised. Moreover, DME selectivity increased a little, because higher temperatures were more favorable for the activity of methanol dehydration catalyst rather than the methanol synthesis catalyst.

Reaction pressure

Figure 7 showed that increasing pressure enhanced the CO conversion due to the increase in reactant (H_2 and CO) concentrations in the reaction environment. Consequently, the rate of the methanol synthesis reaction was enhanced. In addition, since methanol dehydration reaction approached equilibrium, DME selectivity was kept at high levels when the pressure was raised.

Feed flow rate

Figure 8 showed that with increasing the feed flow rate, CO conversion decreased. However, DME selectivity was

Table 4 Catalytic performance of Cu–ZnO–ZrO_2/Al-modified-HM zeolite

Parameter	Temperature (K)	Pressure (MPa)	Flow rate (ml/min)	CO conversion (%)	Selectivity (%)		
					DME	CO_2	Other
Amount	523	5.0	300	68	82	16	2

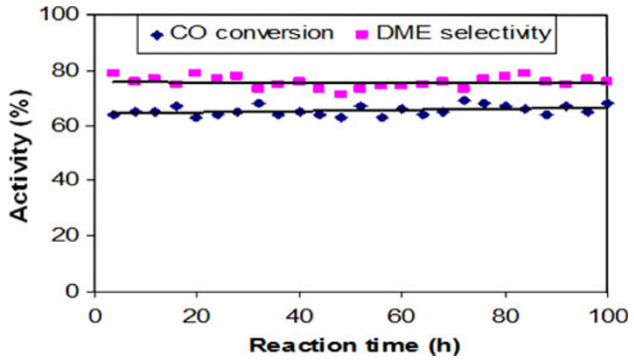

Fig. 5 Variation of activity versus reaction time for Cu–ZnO–ZrO_2/Al–H-mordenite bifunctional catalyst (conditions of catalytic tests were according to Table 2)

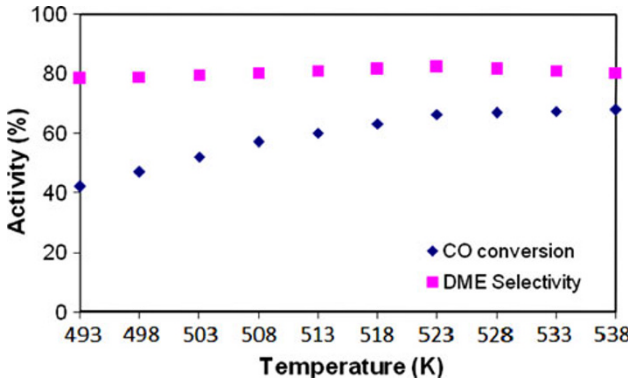

Fig. 6 Effect of temperature on the direct DME synthesis: amount of bifunctional catalyst = 3 g, reaction time = 3 h, pressure = 3.5 MPa, $H_2/CO = 1$, feed flow rate = 200 ml/min

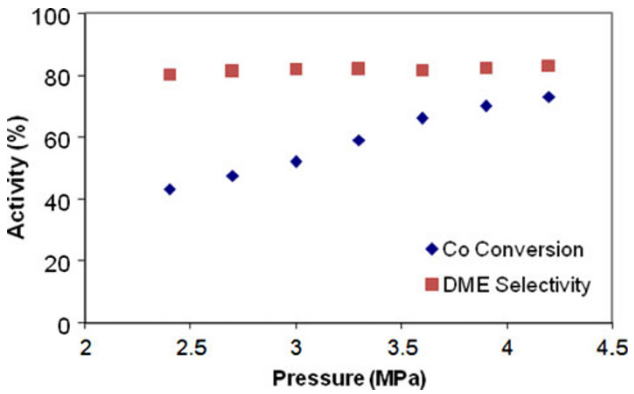

Fig. 7 Effect of the pressure on the direct DME synthesis: amount of bifunctional catalyst = 3 g, reaction time = 3 h, temperature = 523 K, $H_2/CO = 1$, feed flow rate = 200 ml/min

slightly lowered due to higher feed flow rates, which in turn decreased the contact residence time between reactants and catalysts. Obviously, short residence time was unfavorable for DME selectivity, since there was not enough time for the second reaction (syngas to DME) to take place.

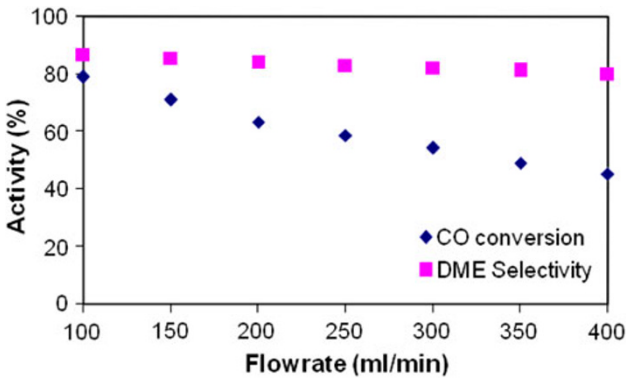

Fig. 8 Effect of the feed flow rate on the direct DME synthesis: amount of bifunctional catalyst = 3 g, reaction time = 3 h, temperature = 523 K, $H_2/CO = 1$, pressure = 3.5 MPa

Therefore, the value of the feed flow rate had to be determined on the basis of DME requirements.

Conclusions

In this study, Al-modified HM zeolite was determined to be an optimum catalyst for dehydration of methanol to DME with high conversion, selectivity and stability. The experimental results showed that Cu–ZnO–ZrO_2/Al-modified H-mordenite was a suitable catalyst for production of DME from synthesis gas. Furthermore, it was demonstrated that optimum temperature for direct synthesis of DME from the synthesis gas was 523 K. Ultimately, it was observed that increasing the pressure enhanced conversion of synthesis gas, while DME selectivity remained constant. In addition, results indicated that increased feed flow rate reduced CO conversion as well as DME selectivity.

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References

Arena F, Barbera K, Italiano G, Bonura G, Spadaro L, Frusteri F (2007) Synthesis, characterization and activity pattern of Cu–ZnO/ZrO_2 catalysts in the hydrogenation of carbon dioxide to methanol. J Catal 249:183

Arkharov AM, Glukhov SD, Grekhov LV, Zherdev AA, Ivashchenko NA, Kalinin DN (2003) Use of dimethyl ether as a motor fuel and a refrigerant. Chem Petrol Eng 39:330

Bivens DB, Minor BH (1998) Fluoroethers and other next generation fluids. Int J Refrig 21:567

Bobbo S, Camporese R (1998) (Vapour + liquid) equilibrium measurement and correlation of the refrigerant (propane + 1,1,1,3,3,3-hexafluoropropane) at T = (283.13, 303.19, and 323.26) K. J Chem Thermodyn 30:1041

Brown DM, Bhatt BL, Hsiung TH (1991) Novel technology for the synthesis of dimethyl ether from syngas. Catal Today 8:279

Fei JH, Yang MX, Hou ZY, Zheng XM (2004) Effect of the addition of manganese and zinc on the properties of copper-based catalyst for the synthesis of syngas to dimethyl ether. Energy Fuel 18: 1584

Ge Q, Huang Y, Qiu F, Li S (1998) Bifunctional catalysts for conversion of synthesis gas to dimethyl ether. Appl Catal A 167:23

Good DA, Li Y, Francisco JS (1999) Location of the first excited states of fluorinated ethers, E143a (CH_3OCF_3), E134 (CHF_2OCHF_2), and E125 (CHF_2OCF_3). Chem Phys Lett 313:267

M He, H Li, T Li, J Wu, Z Liu, J Xi'an (2003) Theoretical analysis of F-methyl methyl ether as a refrigerant of refrigerator. Jiaotong Univ. (Chn.) 37, 10

Jun KW, Lee HS, Roh HS, Park SE (2003) Highly water-enhanced H-ZSM-5 catalysts for dehydration of methanol to dimethyl ether. Bull Korean Chem Soc 24:104

Khandan N, Kazemeini M, Aghaziarati M (2008) Determining an optimum catalyst for liquid phase dehydration of methanol to dimethyl ether. Appl Catal A Gen 349:6

Khandan N, Kazemeini M, Aghaziarati M (2009) Synthesis of dimethyl ether (DME) over modified H-Mordenite zeolites and bifunctional catalysts composed of $Cu/ZnO/ZrO_2$ and modified H-Mordenite zeolite in slurry phase. Catal Lett 129:111

Li JL, Zhang XG, Inui T (1996) Effect of the property of solid acid upon syngas-to-dimethyl ether conversion on the hybrid catalysts composed of Cu–Zn–Ga and solid acids. Appl Catal A 147:23

Li J-L, Zhang X-G, Inui T (1997) Synthesis of dimethyl ether under forced composition cycling. Appl Catal A 164:303

Liu J, Shi J, He D, Zhang Q, Wu X, Liang Y, Zhu Q (2001) Surface active structure of ultra-fine Cu/ZrO_2 catalysts used for the $CO_2 + H_2$ to methanol reaction. Appl Catal A Gen 218:113

Mao D, Yang W, Xia J, Zhang B, Lu G (2006) The direct synthesis of dimethyl ether from syngas over hybrid catalysts with sulfate-modified-alumina as methanol dehydration components. J Mol Catal A Chem 250:138

Qi GX, Zheng XM, Fei JH, Hou ZY (2001) A novel catalyst for DME synthesis from CO hydrogenation 1. Activity, structure and surface properties. J Mol Catal A 176:195

Ramos FS, Duarte de Farias AM, Borges LEP, Monteiro JL, Fraga MA, Sousa-Aguiar EF, Appel LG (2005) Role of dehydration catalyst acid properties on one-step DME synthesis over physical mixtures. Catal Today 101:39

Rhodes MD, Bell AT (2005) The effects of zirconia morphology on methanol synthesis from CO and H_2 over Cu/ZrO_2 catalysts: Part I. Steady-state studies. J Catal 233:198

Rhodes MD, Pokrovski KA, Bell AT (2005) The effects of zirconia morphology on methanol synthesis from CO and H2 over Cu/ZrO_2 catalysts: Part II. Transient-response infrared studies. J Catal 233:210

Suh YW, Moon SH, Rhee HK (2000) Active sites in $Cu/ZnO/ZrO_2$ catalysts for methanol synthesis from CO/H_2. Catal Today 63:447

Sun K, Lu W, Qiu F, Liu S, Xu X (2003) Direct synthesis of DME over bifunctional catalyst: surface properties and catalytic performance. Appl Catal A Gen 252:243

Takeguchi T, Yanagisawa K, Inui T, Inoue M (2000) Effect of the property of solid acid upon syngas-to-dimethyl ether conversion on the hybrid catalysts composed of Cu–Zn–Ga and solid acids. Appl Catal A 192:201

Xia J, Mao D, Zhang B, Chen Q, Tang Y (2004) One-step synthesis of dimethyl ether from syngas with Fe-modified zeolite ZSM-5 as dehydration catalyst. Catal Lett 98:235

Yaripour F, Baghaei F, Schmidt I, Perregaard J (2005) Synthesis of dimethyl ether from methanol over aluminium phosphate and silica–titania catalysts. Catal Commun 6:542